PATENT SPECIFICATION

NO DRAWINGS

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Inventors: JOHN FRAY MEYER and EDMUND JOSEPH ZALEWSKI.

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COMPLETE SPECIFICATION

Polyester-Phenoplast Enamels

We, Schenectady Chemicals Inc., a Corporation of New York, United States of America of Schenectady 1, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyester-phenoplast enamels suitable for application to electrical conductors such as wires (wire enamels) and to electrical conductors having a coating of a said enamel. It is an improvement in or modification of the invention described and claimed in Specification No. 978717.

In Specification No. 978717 there are claimed polymeric esters of terephthalic or isophthalic acid and tris-(2-hydroxyethyl) isocyanurate, compositions containing such polymeric esters and suitable for coating electrical conductors obtained by applying thereto a composition as aforesaid and subsequent heating.

It has now been found that by including a phenolformaldehyde resin in a wire enamel based on a said polymeric ester, wire having a coating of such enamel has good abrasion resistance and improved flexible heat aging and mandrel after snap properties.

According therefore to the present invention there is provided an enamel suitable for use in coating wire conductors comprising a polymeric ester and an amount by weight less than that of the polymeric ester of a phenol-formaldehyde resin, the said polymeric ester being the reaction product of polyhydric alcohol of which at least 10% by weight is tris (2-hydroxyethyl) isocyanurate, and polycarboxylic acid of which at least 20 equivalent per cent is terephthalic acid and/or isophthalic acid.

The polymeric ester referred to may be any such as is described in Specification No. 978717 and may be prepared as described therein. The whole of the disclosure of the said Specification No. 978717, insofar as it relates to the polyesters and their production, is to be regarded as incorporated herein by reference to avoid its repetition in detail.

Specifically, however, it may be noted that in the said polymeric esters at least 50 equivalent per cent of the polycarboxylic acid may be terephthalic acid and at least 50% by weight of the polyhydric alcohol may be tris (2-hydroxyethyl) isocyanurate. Moreover, any part of the polyhydric alcohol which is not tris (2-hydroxyethyl) isocyanurate may be an alkane-diol.

Further, the additives to the wire enamels of Specification No. 978717 described therein may also be included in the enamels of the present invention in analogous proportions. In this connection, where a polyisocyanate is included, as described in Specification No. 978717, it is found that proportions as low as 0.1% may be used to advantage, e.g. 0.1% to 40%, and preferably 0.1 to 15%, by weight of the total solids of the wire enamel.

It has been found that the properties of the polyester wire enamels of the present invention can be improved by incorporating therein a tetrahydrocarbon titanate. Typical titanates include tetraalkyl titanates such as tetraisopropyl titanate, tetrapropyl titanate, tetrabutyl titanate, tetraamyl titanate, tetrahexyl titanate, tetraethyl titanate, tetramethyl titanate and diisopropyl dibutyl titanate as well as carboxylic aryltitanates such as tetraphenyl titanate, tetra tolyl titanate (made from any of the cresol isomers alone or in admixture with each other) and tetraxylenyl titanate.

The titanate may be used, for example, in a proportion .001 to 10%, preferably 1-8%,

[Price

based on the weight of total solids in the wire enamel.

As the phenol-formaldehyde resin there can be used heat reactive condensation products of formaldehyde with phenols such as phenol *per se*, *o*-cresol, *m*-cresol, *p*-cresol, mixed cresols, e.g. cresylic acid and meta para cresol, xylenol, diphenylol propane, *p*-butylphenol, *p*-tert. amyl phenol, *p*-octyl phenol *p,p'*-dihydroxydiphenol ether. Obviously mixtures of phenols can be used as indicated above. There can be used 0.5 to 1.5 moles of formaldehyde per mole of phenol. Preferably less than 1 mole of formaldehyde is employed per mole of phenol. Most preferably about 0.8 mole of formaldehyde is used. The preferred phenol is cresol.

The phenol formaldehyde resin is preformed in conventional manner prior to addition to the polyester.

The solvent employed in making the wire enamel may be cresylic acid. Cresylic acid has a boiling range of 185 to 230°C and is a mixture of *o*-, *m*- and *p*-cresols. The individual cresols, e.g. para cresol, meta cresol or ortho cresol, can be employed although it is preferred to use the commercial cresylic acid mixture.

It is frequently desirable to dilute the cresylic acid with an aromatic hydrocarbon, e.g. a heavy coal tar or petroleum naphtha or with xylene. The naphtha can be employed in an amount of from 0 to 60%, e.g. 5 to 60%, based on the total weight of the solvents, preferably 30-40%. Various conventional aromatic naphthas, especially high boiling naphthas, can be employed such as EW naphtha (an enamel wire heavy coal tar naphtha sold by the Barrett Division of Allied Chemical and Dye Corporation) and Solvesso No. 100, an aromatic naphtha derived from petroleum.

Normally the wire enamel is made up as a 25-50% solids concentration by weight, although this can be varied as desired. The preferred solvent is a mixture of 65% cresylic acid and 35% of an aromatic naphtha.

Preferably the enamel comprises, on a solids weight basis, 75-95% of a polymeric ester of terephthalic acid and tris (2-hydroxyethyl) isocyanurate, 0.1 to 15% of an organic polyisocyanate, 1 to 8% of an alkyl titanate and 1 to 10% of phenol-formaldehyde resin. Within this preferred class of compositions it is preferred that the phenol-formaldehyde resin is made from less than 1 mole of formaldehyde per mole of phenol, that the phenol of the phenol-formaldehyde resin is cresol, and that a portion of the tris (2-hydroxyethyl) is isocyanurate up to 50 equivalent per cent of the total polyhydric alcohol is replaced by an alkane-diol.

The wire enamel is applied to the wire, e.g. copper wire, by either the "free dip" or the die application procedure. In the following specific examples in which wire test results are recorded the die application procedure was employed to obtain a build up of approximately 3 mils on No. 18 copper wire. The enamel was baked on the wire at 750°F.

Typical examples of polyesters suitable for use in the enamels of the present invention are described in Examples 1 to 6 of Specification No. 978717. Another is as follows:—

Polyester Resin A

Tris (2-hydroxyethyl) isocyanurate	4400	lbs.
Ethylene Glycol	481	lbs.
Dimethyl Terephthalate	5019	lbs.
Litharge	4.5	lbs.
Xylol	2173	lbs.

The batch was slowly heated during 8 hours until a temperature of 440°F was attained. There was added a total of 9775 lbs. of cresylic acid and 5265 lbs. of Solvesso 100 to yield a polyester solution having a solids content of 35%.

A typical example of a preferred phenol-formaldehyde resin for use in the invention is as follows:—

Phenol-Formaldehyde Resin B

Meta para cresol	3440	lbs.
37% Aqueous formaldehyde	1962	lbs.
Triethanolamine (catalyst)	64	lbs.

This mixture was heated at reflux for 1.5 hours, cooled to 130°F and 59 lbs. of salicyclic acid added. Vacuum of about 26 inches was then applied and water removed by distillation. The temperature initially dropped to 105°F and then gradually rose to 176°F over a period of 2 hours. The vacuum was stopped, the heat shut off and 4,058 lbs. of cresylic acid added to give an *m-p*-cresol formaldehyde resin solution containing 40% solids.

The following Examples will serve to illustrate the invention. The material MONDUR SH used in these Examples consists of the mixed cyclic trimers of 2,4- and 2,6-tolylene diisocyanates having the three free isocyanate groups blocked by esterification with *m*-cresol.

EXAMPLE 1

The indicated solids were diluted to 30% solids concentration in a solvent containing 65% cresylic acid and 35% Solvesso 100 to make wire enamels which were applied to the wire for testing purposes, (percentages are given by weight).

	a	*b*
Polyester A (at 100% solids)	81.09%	86.14%
Mondur SH	12.97%	4.74%
Resimene 882 (melamine-formaldehyde)	3.89%	—
Tetraisopropyl titanate	2.05%	4.54%
Phenol - formaldehyde		

Resin B (at 100% solids)	—	4.58%
Wire Appearance	Good	Good
Mandrel passed after snap (flex)	3x	2x
Heat Shock 1 hr. at 200°C. 10% stretch	3x	—
Heat Shock 1 hr. at 200°C. 15% stretch	—	2x
Flex heat aging at 175°C.	Fail 24 hrs.	>168 hrs.

The product of Example 1 (b) which is within the invention exhibits superior heat shock and flexible heat aging properties to those of Example 1 (a) which is outside the present invention (but within the scope of the claim of our Specification No. 1046910).

EXAMPLE 2

Polyester A (at 100% solids)	400	grams
Mondur SH	44	grams
Phenol-formaldehyde Resin B at 39% solids in cresylic acid	69.2	grams
Cresylic acid (additional)	684	grams
Solvesso 100	368	grams
Tetraisopropyl titanate	17.76	grams

The wire enamel had a smooth appearance on the wire. The Heat Shock 1 hr. at 2000°C with 15% stretch passed 3x mandrel and the flexible heat aging at 175°C was >96 hours.

EXAMPLE 3

Polyester A (at 100% solids)	400	grams
Mondur SH	44	grams
Phenol-formaldehyde Resin B at 40% solids in cresylic acid	50.4	grams
Cresylic acid (additional)	683	grams
Solvesso 100	367	grams
Tetraisopropyl titanate	10	grams

The coated wire was smooth. The heat shock after 1 hour at 200°C with 15% stretch passed 2x mandrel and the flexible heat aging at 175°C was >144 hours.

EXAMPLE 4

Polyester A (at 100% solids)	400	grams
Mondur SH	12	grams
Phenol-formaldehyde Resin B at 40% solids in cresylic acid	50.4	grams
Cresylic acid (additional)	635	grams
Solvesso 100	341	grams
Tetraisopropyl titanate	17.75	grams

The coated wire was smooth. The heat shock after 1 hour at 200°C with 15% stretch passed 2x mandrel and the flexible heat aging at 175°C was >96 hours.

The words SOLVESSO and RESIMENE used herein are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. An enamel suitable for use in coating wire conductors comprising a polymeric ester and an amount by weight less than that of the polymeric ester of a phenol-formaldehyde resin, the said polymeric ester being the reaction product of polyhydric alcohol of which at least 10% by weight is tris (2-hydroxyethyl) isocyanurate, and polycarboxylic acid of which at least 20 equivalent per cent is terephthalic acid and/or isophthalic acid.

2. An enamel according to claim 1 wherein at least 50 equivalent per cent of the polycarboxylic acid is terephthalic acid.

3. An enamel according to claim 1 or 2 wherein at least 50% by weight of the polyhydric alcohol is tris (2-hydroxyethyl) isocyanurate.

4. An enamel according to claim 3 wherein any part of the polyhydric alcohol which is not tris (2-hydroxyethyl) isocyanurate is an alkane-diol.

5. An enamel according to any of claims 1-4 wherein the phenol-formaldehyde resin is the reaction product of less than 1 mol of formaldehyde per mol of phenol.

6. An enamel according to any of claims 1-5 wherein the phenol-formaldehyde resin is a cresol-formaldehyde resin.

7. An enamel according to any of claims 1-6 which includes 0.001 to 10% by weight based on total solids, of a hydrocarbon titanate.

8. An enamel according to claim 7 wherein the said titanate is an alkyl titanate.

9. An enamel according to any of claims 1-8 which includes 0.1 to 40% by weight of the total solids of an organic polyisocyanate.

10. A wire enamel according to claim 1 comprising by weight on a solids basis 75-95% of a polymeric ester of terephthalic acid and tris (2-hydroxyethyl) isocyanurate, 0.1-15% of an organic polyisocyanate, 1-8% of an alkyl titanate and 1-10% of a phenol-formaldehyde resin.

11. A wire enamel according to claim 10 wherein the phenol-formaldehyde resin is made from less than 1 mole of formaldehyde per mole of phenol.

12. A wire enamel according to claim 10 or 11 wherein the phenol of the phenol-formaldehyde resin is cresol.

13. A wire enamel according to any of claims 10-12 wherein a portion of the tris (2-hydroxyethyl) isocyanurate up to 50 equivalent per cent of the total polyhydric alcohol is replaced by an alkane-diol.

14. A wire enamel according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples 1 (b), 2, 3 or 4.

15. An electrical conductor having a coating of an enamel as defined in any of claims 1-14.

Agents for the Applicants,
V. GALLAFENT & CO.,
Chartered Patent Agents,
8 Staple Inn,
London, W.C.1.

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